presents the possibilities of incorporating experiential regimes as a means to improve the acquisition of students' knowledge.

Yi Wang (2017) examined the impact of integrating augmented reality into the curriculum of a particular university course. The results demonstrated the potential of augmented reality to support students' motivation to learn. According to the author, content based on augmented reality could be used to better support the absorption of learning material.

Augmented reality technology also found its place in displaying facility layout planning, where it was able to put the planned elements into a real environment, as described by the team of Tan et al in their work (2021).

The research team of Wu et al (2021) dealt with methods of image analysis from a mobile phone camera and insertion of 3D models of buildings directly into urban terrain. Wright et al (2020) dealt with the use of virtual reality in urban planning and data visualization for the inhabitants of the region.

In our work, we focus mainly on augmented reality and how it would be perceived by the public.

1.2 *Research goal*

The LIMBRA project is focused on improving students' skills regarding starting a business career. The city of Ostrava has a rich history associated with the mining and processing of minerals. This history is captured in a large number of historical photographs. Since one of the business plans is focused on the use of augmented and virtual reality, we designed and implemented an application on which we were able to display urban data using augmented reality. In order to get feedback from residents on the use of this technology, we have conducted a demonstration to blend the real world with historical photographs using augmented reality application. We created the application as part of the Researchers night event, which is an event directly related to the LIMBRA project. Thanks to the high attendance of this event, we also had the opportunity to get relevant feedback on how this application is perceived by the general public.

2 VISUALIZATION OF URBAN DATA VIA AUGMENTED REALITY

However, in order to perceive augmented reality, mere eyes are no longer enough, but to display this information we must have a device, in this case a camera (sometimes also a mobile phone, projector, smart glasses, etc.). The information added by augmented reality does not occupy a dominant position in the whole space, it is usually information on the edge in terms of topology and meaning, which should not distract from reality, but only complement it appropriately.

At this point, it is worth mentioning the difference between augmented reality and virtual reality, in which all displayed content is already artificially created. In virtual reality, the user is convinced throughout the scene that he is in a different place and in a different space than he actually is. His senses are deceived by virtual reality glasses, or gloves or other devices to fool other senses.

If we want to display an application in augmented reality ourselves, we only need a mobile phone. It contains a camera capable of capturing the surrounding world, a sufficiently powerful processor and software background, as well as a display on which the connection between reality and added elements is displayed. To simplify the process when a mobile phone has to analyze a changing environment, we can use a visual marker. It often has contrasting colors such as black and white ensuring good visibility in various lighting conditions, as well as basic geometric shapes to make it easier to calculate the change in the angle of view of an object relative to the camera. The result is then the display of a 3D object on the marker. However, we do not have to use only mobile phones and tablets to display augmented reality, we can encounter various forms of transparent displays, which can be, for example, part of the windshield of a car. These glasses are also equipped with augmented reality glasses.

The third way to display and perceive augmented reality is a surface projection directly on the object, or holograms projected into smoke and fog, for example. This method has a great advantage because it does not actually impose any requirements on the viewer. The viewer does not need a tablet or glasses and can see the augmented reality with his own eyes.

Figure 1. A view of VSB-Technical University of Ostrava in our augmented reality application.

In our application, we took advantage of the fact that the city of Ostrava has a rich history, captured in many historical photographs. So, we have created an application that can open an imaginary window into the past in some places. For visitors of the Researchers night event and Ostrava residents, we have prepared a smaller exhibition right on the streets of the city. All you have to do is have a mobile phone in your hand, stand in the right place and look around it. Thanks to this, the user is allowed to look at historical photographs that exactly fit into the relief of the surroundings. For the simplicity of the application, we used visual markers and placed them in the vicinity of the VSB - Technical University of Ostrava.

Figure 2. A view of Ostrava city building in our augmented reality application.

The user could download the application to their mobile phone or borrow our tablet with the pre-installed application. After reaching the place, he may point his smartphone at the object and could look around the place in the past. The illusion of immersion in historical photography is, of course, limited by photography width itself. However, the edges of historical photography fit to the edge of the real-world surroundings.

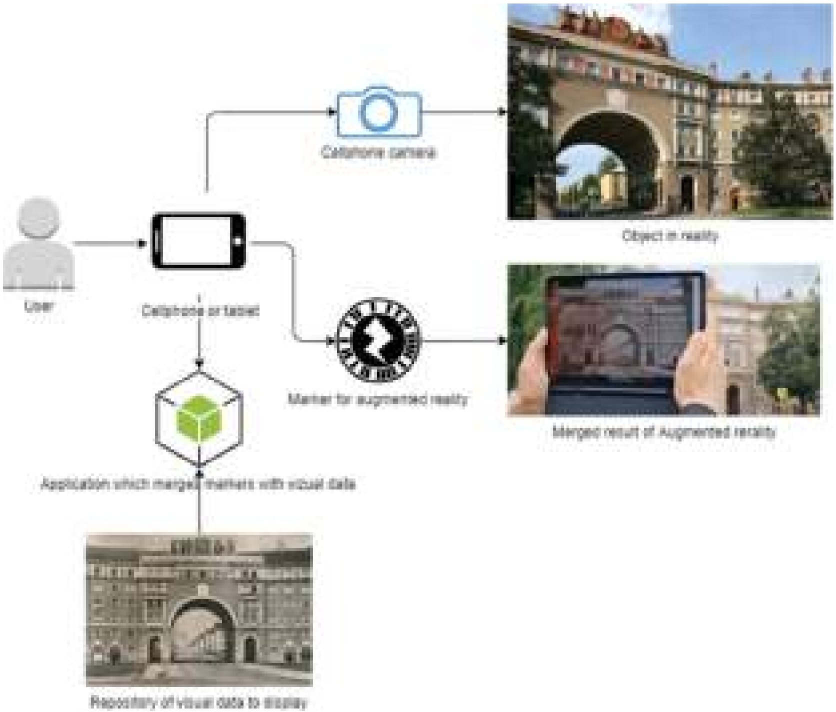

Figure 3. The principle of augmented reality visualization.

Figure 4. Augmented reality used for future construction plans.

The application works on both Android and iOS mobile phones. The application uses the camera of a mobile phone to obtain an image of the surroundings. The image is then analyzed and the presence of a visual marker is sought in it. If a marker is found, the application reaches its database and displays the appropriate visual element overlaying the marker. The result is a visual illusion for the viewer on the user's mobile phone display, combining the added content with a real camera stream.

We tried to show that we can look to the future in the same way and, for example, have life-size plans for future construction visualized on an empty grassy area and see how the construction would affect the peculiarity of the surroundings.

3 SURVEY AND RESULTS

During the Researchers Night we gathered data of 50 respondents from the group of Researchers Night visitors to get feedback about the experimental augmented reality application. The data were connected to the abilities of general public in the area of smart technologies, abilities to interpret classic technical documentation and construction planes, perception of the presented application as well as further possible optimization of the application.

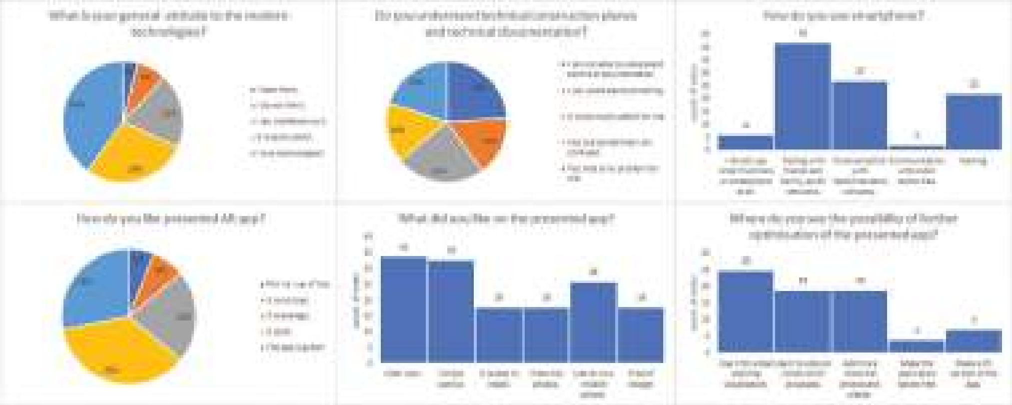

Figure 5. All age groups together.

According to the analysis of the gathered data we found a significant differences between age groups, so we decided to split the results and describe each age category separately.

As we can see on the graph (Figure 6) the respondents in the age group 0-6 years are very open to new technologies although they are not able to understand technical documentation. They also often do not use smartphones but when they do, they use it for gaming or for social networks browsing. Despite all possible problems this age group generally likes the new application.

As we can see on the graph (Figure 7) the respondents in the age group 7-20 years are also open to new technologies, but they are better in understanding of technical documentation of construction. In addition to previous age group, they use smartphones often for social networks, communication with friends, family, and sometimes public institutions like banks. This age group also generally likes the new application; however, some respondents found the app not so interesting. This age group also recommends using similar applications for urban planning visualizations as well as to add a voting function.

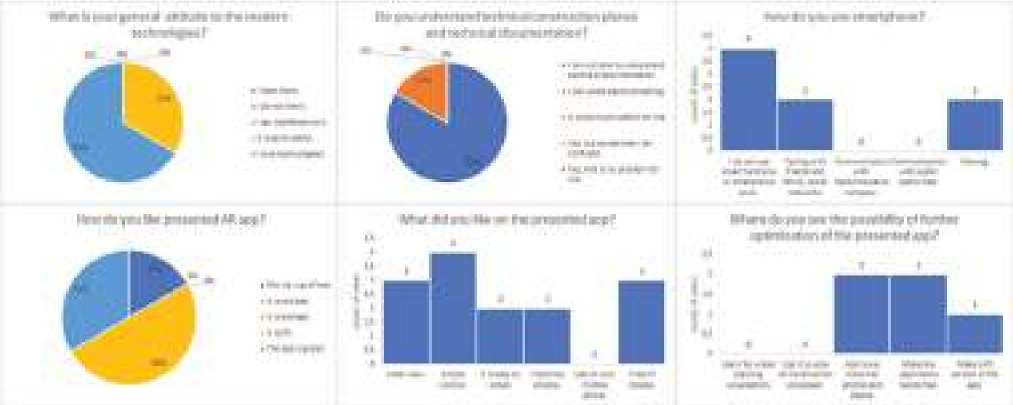

Figure 6. Age group 0-6.

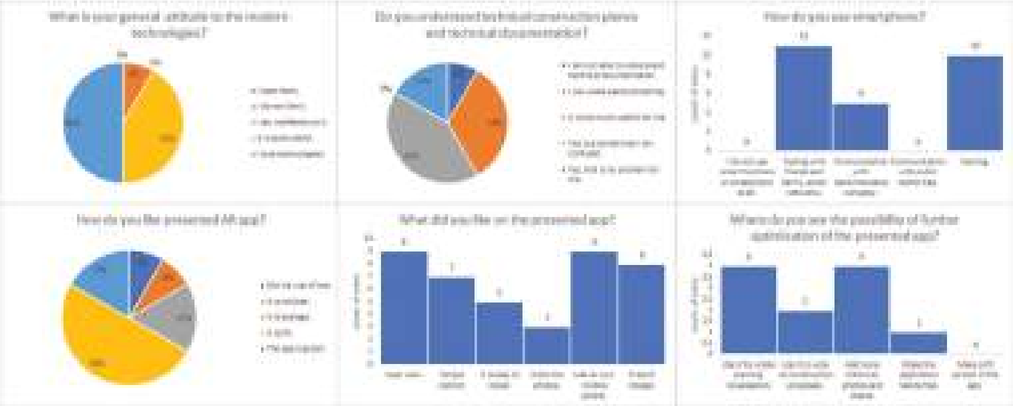

Figure 7. Age group 7-20.

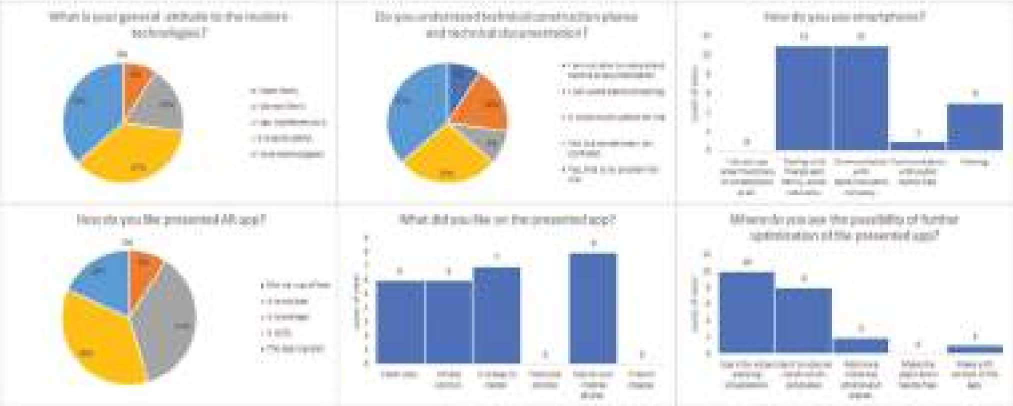

Figure 8. Age group 21-35.

In the age group of 21-35 quite a lot of respondents (64%) said that they can easily or with some minor complications understand technical plans and construction documentation but despite this fact they would recommend tested application to be used for urban planning visualization instead of classic plans publication.

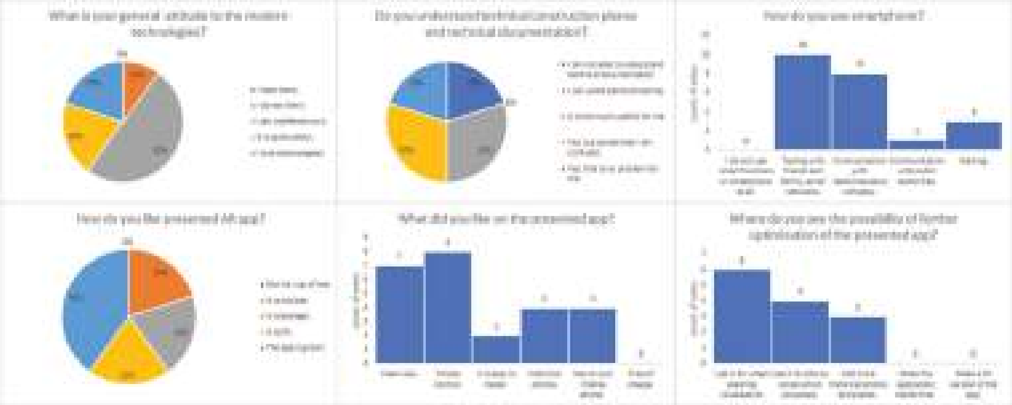

Figure 9. Age group 36-50.

In the age group of 36-50 quite a lot of respondents (50%) said that they can easily or with some minor complications understand technical plans and construction documentation but despite this fact they would recommend tested application to be used for urban planning visualization instead of classic plans publication. Members of this age group enjoyed the simple control of the app however half of the group specifies it’s attitude to the modern technologies as indifferent.

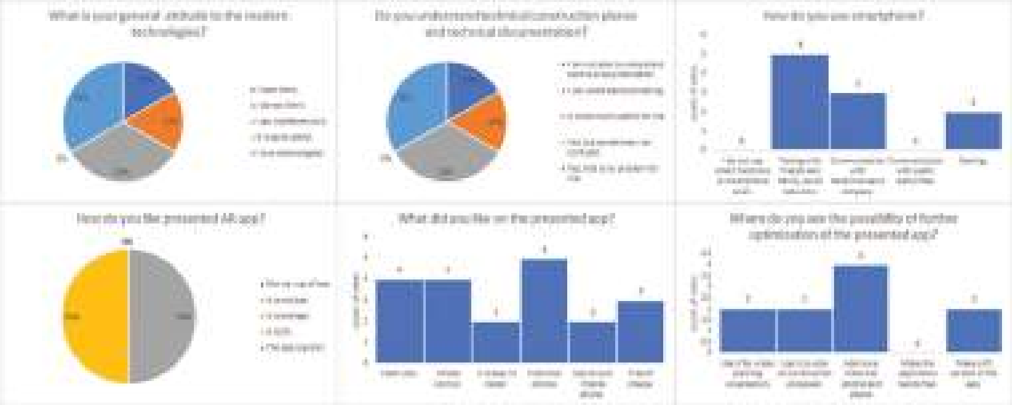

Figure 10. Age group 51-65.

In the age group of 51-65 we lack a previous enthusiasm with the app, the users thought the tested application is average or “Just OK”, but as a new phenomenon they enjoyed the fact that the app is free to try and that it has some historical photos that remind them their past years. They also suggested to develop these historical photos aspect in particular.

As we can see on the graph (Figure 11), with the last age group we got back to the stage when not much smart functions on phones are used (only social networks and communication with friends). The application was still accepted well especially for its clear view and simple controls. Historical aspect was favorited even more here as well as the possibility to add more such historical backgrounded pictures.

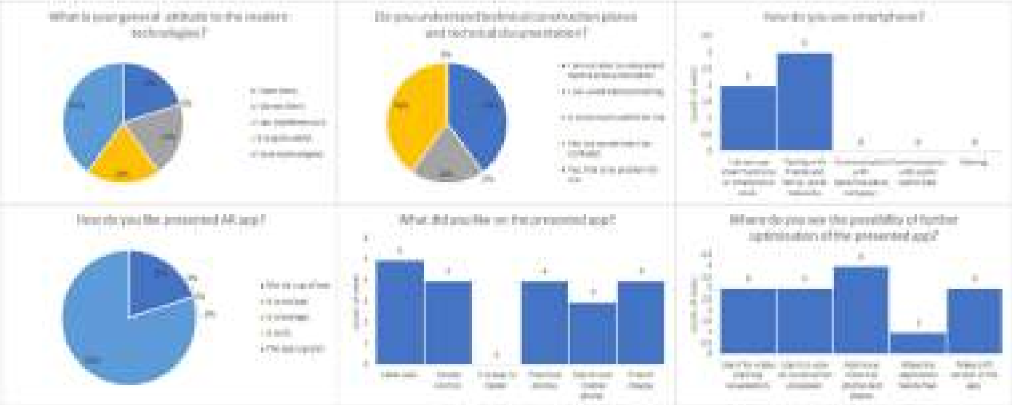

Figure 11. Age group 66+.

4 DISCUSSION OF RESULTS AND CONCLUSION

The results of the questionnaire survey showed that the offered method of displaying augmented reality is generally well accepted among the visitors of VSB-TUO part of Researchers Night. People welcomed the use of their own mobile phone as a tool to investigate the augmented reality layer. Respondents find the application clear, simple, and easy to use, even for older age groups. They could imagine that with a similar application, they would be able to look at real land use plans. They would also welcome the opportunity to vote on the possibilities of the planned construction. According to the respondents, such a vote should have an advisory power in the actual decision-making of the city or regional council.

However, markers used in this implementation, do not exist in the ordinary world, so we would like to extend this application in another direction. In the future the image database could be loaded based on the GPS position of the mobile phone, and a constant visual element in the shot would serve instead of a marker to merge the augmented reality with the surroundings. Further steps in solving this issue would lead to cooperation with city districts and the submission of a joint project to visualize land use plans using augmented reality with the possibility of participation of citizens living in the locality in the choice of modifications and expansion of urban development by voting directly in the application.

Probably since the Moravian-Silesian region is historically associated with mining activities, it was often said that this method could be used to visualize plans for reclamation of the landscape after coal mining and the decline of heavy industry in general.

REFERENCES

Fernandez, Manuel. 2017. Augmented-Virtual Reality: How to improve education systems. Higher Learning Research Communications. 7. 1. 10.18870/hlrc.v7i1.373.

Tan, C.H., Yap, H.J., Musa, S.N. et al. 2021 Augmented reality assisted facility layout digitization and planning. J Mech Sci Technol 35, 4115–4123. https://doi.org/10.1007/s12206-021-0823-6

Vergara, Diego & Extremera, Jamil & Rubio, Manuel & Dávila, Lílian. 2019. Meaningful Learning Through Virtual Reality Learning Environments: A Case Study in Materials Engineering. Applied Sciences. 9. 1–14. 10.3390/app9214625.

Wang, Yi. 2017. Using augmented reality to support a software editing course for college students: Augmented reality for educational applications. Journal of Computer Assisted Learning. 33. 10.1111/jcal.12199.

Wright, Jessica & Gopal, Sucharita & Ma, Yaxiong & Phillips, Nathan. 2020. Seeing the invisible: From imagined to virtual urban landscapes. Cities. 98. 10.1016/j.cities.2019.102559.

Yong Wu, Weitao Che, Bihui Huang. 2021. "An Improved 3D Registration Method of Mobile Augmented Reality for Urban Built Environment", International Journal of Computer Games Technology, vol. 2021, Article ID 8810991, 8 pages, https://doi.org/10.1155/2021/8810991

Entrepreneurship in the Raw Materials Sector – Bartha et al. (Eds)

Coal-fired power plants in the crossfire of the European Union's energy and climate policy

Á. Horváth, A. Takácsné Papp & P. Bihari
University of Miskolc, Miskolc, Hungary

ABSTRACT: For decades, the European Union has taken decisive actions through its energy and climate policy in order to shift its energy mix from fossil fuels to renewable energy sources. In 2017 the policymakers decided to remove coal from the energy mix in order to achieve the climate goals. Most member states have already announced the last date of coal phase-out. In the year of the Paris Agreement (2015) the EU28 had 292 coal-fired power plants working with 758.5 million tonnes of CO_2 emission in a year. (CarbonBrief.org) According to our calculation, four large companies are responsible for 40.5% of CO2 emission. Our article focuses on the effects of the coal phase-out on the operation and future strategy of these companies, used mostly the annual reports as sources. Our findings are summarised in case studies. Although coal phase-out severely affects these companies, it does not shake their operation. The strategies using by the companies are mostly proactive and similar in the main principles. They want to be leaders rather than sufferers of the transformation of the energy system.

1 INTRODUCTION

Nowadays anthropogenic activity causes an enormous environmental and climate pollution that has catastrophic consequences for our planet. Humanity has reached a significant turning point. In order to leave a liveable Earth for our children, an urgent change is needed in people's mind and behaviour. The Paris Agreement (which was signed in 2015) is a milestone in climate protection. 195 countries expressed their commitment against global warming (UNFCCC 2021). Energy production and consumption can play a significant role in achieving these goals because these sectors account for more than 75 percent of the total CO_2 emissions, most of which are emitted by oil and coal combustion (Eurostat, 2021)

From the countries who signed the Paris Agreement, only the European Union took decisive actions regarding the coal phase-out process, so this paper focuses only on EU 28.

The policymakers of the European Union decided to remove coal from the energy mix in order to achieve the climate goals a couple of years ago. According to the Powering Past Coal Alliance (PPCA) launched at COP23 in 2017, a coal phase-out is needed by 2030 in the OECD and in EU28, and by 2050 in the rest of the world (PPCA, 2021). As one of the pioneers of climate protection, the EU has set increasingly ambitious goals in its energy and climate strategy for 2020, 2030, and finally to achieve carbon neutrality by 2050. Most member states have already announced the final deadline for coal phase-out. In August 2021, nine member states had no carbon in their energy mix or had already reached the coal-free status. Seven countries in the EU plan to phase-out coal from their electricity generation by 2025 and another five by 2030. Germany, however, has set a deadline for 2038, probably they will try to

DOI: 10.1201/9781003259954-16

Table 1. Summary of national coal phase-out announcements in the EU member states - as of August 2021.

Category	Number of countries	Country names
Coal-free	3	Belgium (2016), Austria (2020), Sweden (2020)
Phase-out by 2025	7	Portugal (end-2021), France (2022), United Kingdom (2024), Hungary (2025), Italy (2025), Ireland (2025), Greece (2025)
Phase-out by 2030	5	Denmark (2028), Finland (mid-2029), The Netherlands (end-2029), Slovakia (2030), Spain (2030)
Phase-out after 2030	1	Germany (end-2038)
Phase-out under discussion	4	Czech Republic, Slovenia, Romania, Croatia
No phase-out discussion	2	Bulgaria, Poland
No coal in electricity mix	6	Cyprus, Estonia, Latvia, Lithuania, Luxembourg, Malta

Source: Europe Beyond Coal, 2021a

finish the phase-out process sooner. Negotiations regarding decarbonisation are still ongoing in four member states, and there are only two countries where the issue has not been discussed yet (Europe Beyond Coal, 2021a).

In the year of the Paris Agreement (2015) the EU28 had 292 coal-fired power plants working with 758.5 million tonnes of CO_2 emission in a year. Thanks to Europe-wide regulations in the last 5 years, 61 power plants were retired from operation and a lot of them were upgraded so the yearly emission decreased to 338 million tonnes of CO_2.

However, some of the countries still have a big chunk of coal plant based energy in their energy mix (Germany or Poland), although their effort to reduce the environmental impact is undeniable.

2 LITERATURE REVIEW

The literature review shows that the topic is quite current and popular among the authors. Numerous papers deal with the analysis of the legal and political framework and impacts of the coal phase-out in different countries (Lund, 2017 (Finland), Heinrichs and Markewitz, 2017 (Germany), Rentier et al., 2019 (UK, Germany, Spain and Poland), Akerboom et al., 2020 (The Netherlands), Osorio et al. 2020 (Germany), Brauers-Oei, 2020 (Poland), Brauers et al. 2020 (UK and Germany), Markard et al. 2021, (Germany)). Each country had different starting point in terms of its energy mix, available energy sources and the targets set, etc.) and had diverse motivations and legal frameworks for implementing the coal phase-out plans.

Several articles attempted to estimate and quantify the environmental, economic and social impacts of the coal phase-out. One of the important questions is, how could the so-called "waterbed effect" could be avoided. This may occur, when the sale of emission allowances from CO_2 savings increases CO_2 emission elsewhere, so the overall CO_2 emissions will not decrease. The thoughtful design of the EU-ETS rules (especially the regulations on the emission ceiling and the market stability reserve) play an important role in the mitigation of these effects. (Osorio et al. 2020) In addition to the environmental impacts, the analysis of the social and economic effects is also very important. Coal phase-out has significant costs and burdens, but perceptible cost savings and economic benefits can also be realized. Analysts come to different conclusions when analyzing the costs and benefits of the coal phase-out, if they take into account not only the costs but the social impacts in their calculations. Such social impacts can be eg. the saving of environmental and health costs through avoided CO_2 emissions, or addressing employment problems in coal regions, etc. Studies show that it would be important, but at the same time it is difficult to find a balance between environmental, economic and social aspects. The coal phase- out must be implemented keeping the principles of the just transition (Van den Bergh-Botzen, 2015; Chan et al., 2017; Akerboom et al., 2020; Keles-Yilmaz, 2020; Heinisch et al., 2021).

Other studies focus on the profitability of power plants, and the impacts of coal phase-out on profitability. Carbon Tracker (2018) analyzed the profitability of 6,685 coal-fired power plants worldwide and highlighted that approximately 42 % of the plants operated at a loss in 2018. The authors estimated the proportion of loss-making coal-fired power plants at 56 % by 2030 and 72 % by 2040. A similar conclusion was reached by Edis-Bowyer (2021) who argued that by 2025, the economic viability of several Australian coal-fired power plants would become questionable as a result of increasing renewable energy production, so shutdown could be an attractive or even inevitable option for these power plants. In 2020 Gillich et al. analyzed the effects on the contribution margins of power plant owners, separating the effects of coal phase-out, CO_2 prices and the growing share of various renewable energies. One of the main conclusions of the study is that "Contribution margins can vary greatly between technologies and plants using the same technology" (Gillich et al. 2020, p. 9), the scenarios examined by the authors showed a difference of up to 9.5-fold in the cumulated contribution margin in the period 2020-2050 between old and new power plants. In addition, the study found that "The influence of a coal phase-out on the cumulative contribution margin of a power plant in real value can be between 5 and 47%, depending on the extent of the renewable energy expansion and the level of the CO2 price." (Gillich et al. 2020, p. 9)

3 METHODOLOGY

The cumulated relative CO_2 emission of the power plants was investigated in breakdown by owners in the European Union in 2015, in the year of the Paris Agreement. The analysis is based on the European Coal Plant Database, which contains data of 292 coal-fired power plants (EU28). The results of the study made it clear that only four large companies (with their 60 coal-fired power plants) are responsible for 40.5% of the CO_2 emissions in Figure 1. This research examines these companies through the review of their annual reports and other official documents, which are available on their official website.

The methodological framework of our study is basically descriptive and uses case study method.

The focus of our data collection was on the following points:

- the main activities of the companies,
- countries, where the company is active,
- energy mix and power plant portfolio of the company – installed capacity and power generation by sources,
- number of hard coal- and lignit-fired power plants,
- market conditions – challenges on the energy market,
- context of the mention of coal phase-out,
- regulatory environment (EU regulation and country-specific regulation),
- strategies and schedule for coal phase-out in case of power plants,
- CO_2 emissions,
- profitability and financial situation of the company, especially for conventional power generation,

Because of the different structure and content of the annual reports, it was difficult to use the same approach in a consistent way for all of the companies. The research questions were:

- how their operation was affected by the coal phase-out plans and the ongoing energy transition in the European Union,
- what pathways and solutions they have chosen,
- what strategy they have created to ensure their future survival,
- and last but not least, whether is there any shift in their emission levels compared to 2015.

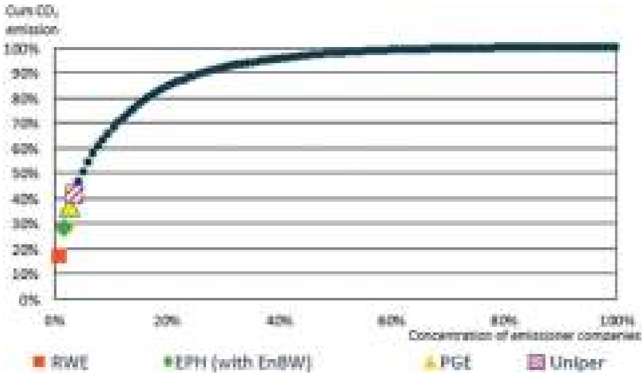

Figure 1. Cumulated relative CO_2 emission of the power plants by owners (n=126) in 2015.
Source: Own elaboration based on Europe Beyond Coal 2021b

4 CASE STUDIES

The International Energy Agency's report on the electricity market 2021 highlights that despite numerous revenue generation opportunities (forward contract, day-ahead and intraday markets, market balancing and capacity remuneration) energy companies owning coal-fired power plants faced a number of difficulties in recent years. The ever-changing legal framework and market conditions make the operation of coal-fired power plants difficult. These processes are increasingly affecting power plants operating with less efficient and emission-intensive technology. On the other hand, coal-fired power plants have an increasingly important role in the system stability because renewable energy generation alone is not able to maintain system stability (IEA, 2021). This section summarises the pathways and strategies of the four most polluting companies operating in the European Union related to the coal phase-out plans.

4.1 *The RWE group*

RWE is one of the largest energy companies in Europe. It is active at all stages of the energy supply chain, including energy production, energy distribution and energy trade. The focus of its activities has been continuously changing as a result of the major energy market events of recent years and the increasingly strict climate protection regulations. By 2020, it has become one of the world's leading renewable energy companies. "Our energy for a sustainable life" is how the company defines its strategic goal. Their ambition: "We will be carbon neutral by 2040, with clean, secure and affordable energy." This idea has gradually matured into the company's main strategic goal in recent years. The power plant portfolio of the company and the energy mix of electricity generation changed significantly between 2015 and 2020. Both the installed capacities and the amount of electricity produced decreased during this time. The installed capacity of hard coal-fired power plants was significantly reduced by 2020 (Figure 1). As a result of that also the amount of electricity generated in coal-fired power plants was reduced (Figure 2). The installed capacity of lignite-fired power plants decreased to a lesser extent (see Figure 2), but it can be seen that the amount of energy they produced decreased significantly (Figure 3). This was due to the fact that most of these power plants did not operate at full capacity. Several of them operated as a reserve to balance fluctuations in the system caused by renewables, and several power plants were switched to standby operation as a result of legal regulations. The role of nuclear energy has diminished as a result of the German nuclear phase-out. The growth of renewable energy sources is remarkable - the installed capacities increased from 4,146 MW (2015) to 10,148 MW (2020) within 5 years. 84.1 % of renewable capacities are represented by wind farms (65.2 % onshore wind, 18.9 % offshore wind).

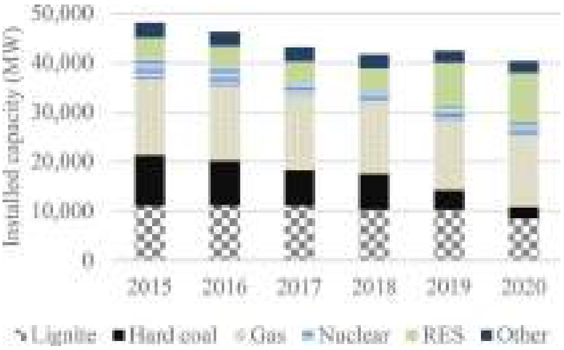

Figure 2. Installed capacity by sources of energy at RWE, 2015-2020.

Source: Own elaboration based on the annual reports of the RWE Group 2015-2020

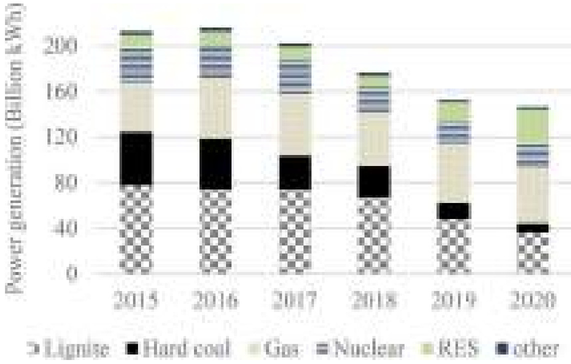

Figure 3. Power generation by sources of energy at RWE, 2015-2020.

Source: Own elaboration based on the annual reports of the RWE Group 2015-2020

The ratio of solar energy is 2.1 %, and hydropower and biomass account for 13.8 % in the renewable mix of the company.

According to the European Coal Plant Database (Europe Beyond Coal, 2021b.) 9 lignite-fired power plants (with 42 units) and 11 hard-coal fired power plants (with 30 units) are in the ownership of the RWE Group. Geographically, the company has coal-fired power plants in Germany (56 units, of which 15 are hard coal-fired, and 41 lignite-fired), in the United Kingdom (10 units, hard coal-fired) and in the Netherlands (5 units, hard coal-fired). In addition, the Mátra Power Plant, the lignite-fired power plant of Hungary was majority-owned by RWE until its sale in 2017. Of the 72 units, 30 were already retired by the end of 2015. Between 2016 and 2020, 8 units were retired, of which 7 were hard coal-fired (Europe Beyond Coal, 2021b). By 2021 (earlier than originally planned), RWE had completely phased out the hard coal-fired electricity generation in the UK and Germany. The remaining two plants in the Netherlands are being converted to biomass (Amer 9 and Eemshaven). From 2021, lignite-fired units will also be phased out gradually, in the Netherlands by 2029, and in Germany by 2038 (RWE Annual Report 2020).

The ever stringent regulatory environment accelerated the coal phase-out process during the examined period. In addition to the Paris Agreement, EU Winter Package, EU-ETS rules, and Green Deal, a number of regulations at national level were mentioned in the RWE's annual reports. One of the important regulations is the planned criteria for power plants' GHG emission, excluding coal-fired power plants from the capacity auction market. The company faces different regulatory environments in Germany, UK and the Netherlands. Some examples can be listed for each country. In Germany RWE has had to take 5 lignite-fired power plants into stand-by operation (and later shut down) in exchange for a compensation. The Coal Phase-out Act of 2020 envisages the German coal phase-out by 2038 and determines the road map for the shutdown and the compensation schemes for lignite and hard-coal-fired power plants. In the case of the United Kingdom the introduction and operation of the capacity market and the climate change levy imposed on fossil fuels were mentioned in the annual reports. In the Netherlands coal phase-out is planned by 2030, without providing compensation to power plants. The introduction of a carbon price floor is a special idea in this country (RWE Annual Reports 2015-2020).

The company uses three types of strategies for coal phase-out in the case of its power plants. The most commonly used strategy is the plant-closure (immediately or after a standby operation period). There were also examples of selling RWE's shares to another company (e.g. Mátra Power Plant). Finally, a possible solution is to switch the plant to another alternative fuel, as in the Netherlands, the last two plants will be converted to biomass-fired. The chosen strategy and timing are influenced by several aspects, such as the regulation of the given country, the age, technology, profitability and efficiency of the power plant. As mentioned, RWE had completely phased out its power generation from hard-coal by 2021, earlier than originally planned. This was largely due to the specific design of the German compensation scheme for early phase-out, which encouraged the company to make use of the opportunities for compensation in the first line. As we have seen, a significant expansion of renewable energy production will play a prominent role in the strategy of the company. It also wants to maintain its position in underpinning the security of supply, by making available its flexible (predominantly gas-fired) power plants available. The company spends huge amounts on innovation in many areas, such as storage technologies or green hydrogen. RWE has chosen a proactive strategy and wants to be a leader rather than a sufferer of the transformation of the energy system (RWE Annual Reports 2015-2020).

The CO_2 emissions of the RWE Group decreased by about 41 percent globally, from 150.8 million metric tonnes to 88.1 million metric tonnes during the 5 year period under review. Also the specific emission (i.e. in carbon dioxide emissions per megawatt-hour of electricity generated) has been reduced significantly (from 0.708 metric tons to 0.47 metric tons) from 2015 to 2020 (RWE Annual Reports 2015-2020).

The example of RWE showed that although coal phase-out severely affects the company, it does not shake the operation of the firm and due to its graduality, did not provoke strong protests from the company. This may have been due to the fact that the period from 2015 to 2017 was critical for conventional electricity generation (RWE Annual Reports 2015-2017). The margins of power generation (wholesale electricity price decreased by cost of fuel and quota prices) was low and had a declining tendency. Some power plants could not cover their operation (fixed) costs because of low utilization and had to be shut down temporarily. Under these uncertain and insufficient profitability prospects, the company was not shocked by the requirement of the gradual exit from coal-based power generation.

The regulations affect the financial situation of the company in different ways. To name just a few examples: The lignite phase-out put a significant financial burden on the company. Although, the firm will receive a compensation of 2.6 billion euros in exchange for the early phase-out based on the negotiations, the company believes that this amount will not cover their real burden. The expected redundancies in the lignite business will affect more than 3,000 jobs in the near future, which could increase to 6,000 by 2030. The government must find socially acceptable solutions for the regions and employees concerned. In the first German coal phase-out auction RWE had a winning bid for the early shutdown of its last 2 hard coal-fired power plants, resulting in a compensation payment of € 216 million. In the Netherlands, there is no compensation for the shutting down of power plants. The last two power plants owned by the RWE Group will be converted to co-fire partly with biomass, with the help of a state aid of € 2.6 billion for 8 years. The subsidy covers investment costs as well as the differences in the cost of fuels. A full conversion to biomass would result in substantial additional burdens. As no further support is provided by the state, RWE is considering legal action to compensate for its damage (RWE Annual Reports, 2015-2020).

4.2 *EPH group*

Before the Paris Agreement came into action the Czech-based Energetický a Prùmyslový Holding (EPH/EnBW company included) was the second largest company in the EU based on the annual CO_2 emission by coal-fired power plants, with its 86 million tons emission. Thanks to the regulations of the European Union, this number has significantly decreased in the last 5 years (EU-wide). However, EPH still remains amongst the top emissioners with its 55 million tonnes of CO_2 emission and with 13 operating plants.

The energy portfolio of the company is quite diversified. As Table 2 shows, the annual income of the EPH from gas and heat fired energy production had been increasing unbrokenly till 2020, when they had a sudden drop due to the pandemic, while revenues from coal-based energy production were very fluctuating.

Table 2. Annual income of EPH group between 2015 and 2020 by energy carriers (in million euro).

Energy carrier/ Year	2015	2016	2017	2018	2019	2020
Gas	*1581*	1675	1989	2156	2342	2201
Heat	*298*	358	345	354	395	329
Coal	*289*	268	294	337	250	210

Source: Own elaboration based on Annual reports of EPH 2015-2020

The sudden change of the revenues from coal-fired energy production in 2017-2018 can be explained by the variability of wholesale prices rather than by the decrease in the volume produced.

Analyzing the annual reports of the company between 2015 and 2020, we can see that the year by year environmental impact of their operations has been playing a more and more considerable role in their agenda. In 2015 it contained only a couple of pages about the environmental aspects of their operations and it was also mentioned that although they did not have a group-wide environmental initiative, the company was committed to meeting all the requirements of the EU and also complying with each country's regulations where they operate. In contrast, five years later, in 2020, their annual report contained approximately 30 pages about their effort related to environmental protection and they had a clear strategy for the future. „We continue to deliver on our strategy of steady carbon footprint reduction while providing flexible generation capacity and full security of energy supply." (EPH annual report 2020. p.7)

Of course, while companies are committed to decreasing their greenhouse-gas emissions, their main goal is to have a profitable business, so the economic impacts have to be aligned with the environmental protection goals. For example, in 2017 coal prices rose sharply due to the massive need for China's plants, thus energy production from coal became more expensive, giving more space to gas electricity generation in Europe.

The regulations of the European Union in the last years were also effective so the energy companies started to reduce their CO_2 emissions and invest money into zero carbon emission processes, such as biomass power plants. EPH Group is also not an exception from that. Between 2015 and 2018, they invested more than 850 million euros in zero or low carbon emission generation capacities and their Lynemouth plant belongs to the largest biomass power plants in the EU saving the globe from more than 2.7 million tons of CO_2 annually

Table 3. Most important financial KPI's and the number of employees of EPH group from 2015 to 2020 (EBITDA and EBIT are in million euro).

Key KPIs	2015	2016	2017	2018	2019	2020
EBITDA (million euro)	*1637*	1 520	1819	1743	2051	2150
EBIT (million euro)	*1382*	966	1346	1190	1396	1376
Employees	N/A	10310	10237	10711	11454	11281

Source: Own elaboration according to the Annual Reports of EPH 2015-2020

It is also important to note, that while they are investing a vast amount of money into zero carbon emission, their business could remain successful in the last years, not only financially (EBIT) but socially (number of employees) too (EPH annual reports 2015-2020).

4.3 *The PGE group*

Out of the 13 operating coal-fired power plants of the PGE Group, only 2 have a retirement date yet. One of their ~~plants~~ in Czechnica will be retired in 2023 (announced in 2019) and the other one in Belchatow will be retired in 2036 (announced in 2021). However, it is true that the Belchatow plant accounts for more than 50% of the CO_2 emission of the PGE's operating capacities.

This dependency can be seen in their Annual Reports between 2015 and 2020, because there is no further discussion about the Paris Agreement, nor about the coal phase-out strategy connected to their portfolio. The only highlighted information in their reports, which is related to environment protection, is that they are constantly trading CO_2 rights and they are really thorough about the financial impacts of the future price changes in ETS or in raw materials (coal) (PGE annual reports 2015-2020).

Although, they do not mention coal phase-out in their reports between 2015 and 2020, they announced their new corporate strategy in October 2020, which set the tone for the future changes with a 75 billion PLN CAPEX budget for the 2021-2030 period, of which they are planning to spend more than 50% for renewable energy sources.

As part of their strategy and in alignment with the EU expectations, they seek to decrease the company's CO_2 emission by 85% by 2030 and achieve climate neutrality by 2050. For that, it is inevitable to convert their coal heated power plant capacities to gas fired or biomass fired capacities. The main financial sources of their future plans are:

- Cohesion Policy
- Recovery and Resilience Facility
- Just Transition Fund
- React EU
- Invest EU
- Innovation Fund
- Horizon Fund
- and of course loans from private and public sources.

As it can be seen, they are highly depending on the money, which can be obtained from the European Union, and they openly admit, that at least 25% of the money has to come from funds, otherwise their operation cannot be maintained or the goals cannot be achieved (Decrease CO2 emission by 85% till 2030) (PGE Group Strategy 2030).

However, they clearly expressed their need for non-refundable money, for 2025, they are calculating with more than 5 billion PLN EBITDA/year and with more than 6 billion PLN EBITDA/year after 2030. „The goal of the PGE Group is a full use of dedicated financing options for green investments and off-balance sheet financing." (PGE group Strategy 2030 page 35.**)**

4.4 *The Uniper group*

The Uniper Group was established in 2016 when it separated from the E.ON Group. (Uniper, 2016a.) Nowadays it is one of the leading energy companies in the world's 40 countries. In 2020, it had around 12,000 employees. The company has three core business segments namely the European Generation (most significant segment), Global Commodities and the Russian Power Generation. Between 2016 and 2020 the company operated its coal-fired power plants to produce power and heat in Germany, in France, in the Netherlands, and in the United Kingdom within the border of the European Union and in the frame of the European Generation segment. A significant part of the generated energy is transferred to the Global

Commodities segment, and the other part is sold through long-term electricity and heat supply contracts. Climate change is one of the most important priorities of Uniper's strategy (Uniper, 2020a.). The European Green Deal, besides the provisions of national law, jeopardize the profitability of the company under the current operating structure because its coal-fired power plants were the fourth largest polluters in the European Union in 2015 (Europe Beyond Coal Database, 2021b). In response to the changing market and regulatory conditions, the Uniper Group decided to become carbon-neutral by 2035 in Europe, and in all segments by 2050. In 2020, Uniper announced its phase-out plan which frees the environment from 18 tons of carbon dioxide per year (Uniper 2021a.). The company marked out the path to reaching carbon neutrality by 2050. In this way, not only does European production play a prominent role, but it also covers all business segments of Uniper (Russian Power Generation and Global Commodities). First, it will decrease its CO_2 emission by 2030 compared to the 2019 level, and finally it will reach complete carbon neutrality in the European Generation segment by 2035. (Uniper, 2020b) Its carbon intensity decreased by 10%, and the direct carbon emissions from fuel combustion fell by 41% between 2016 and 2020 (Uniper, 2020a.). In the European Generation segment, nitrogen-oxide (NOx) decreased by 48%, sulphur-dioxide (SO_2) by 78%, and the dust emission by 62% (Annual Report of Uniper 2018, Uniper 2020b.)

According to Figure 4, the energy mix of the electricity production was mostly based on hard coal and lignite (43%) in 2016. This ratio decreased to 27 % by 2020 due to the circumstances mentioned above. During the examined period only one plant unit used lignite (Schkopau A +B), the other power plants burned hard-coal. The average age of the plants was 43 years.

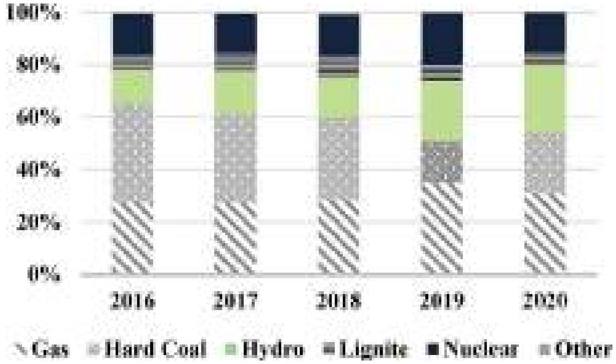

Figure 4. Uniper's energy mix of electricity production.

Source: own elaboration based on Uniper's Sustainability Reports 2016-2020

The European and national coal phase-out strategies pose a huge challenge to the company. According to Uniper's official documents, five directions of its carbon phase-out strategy can be distinguished:

- further operation (Datteln IV., in Germany)
- further operation as a reserve power plant (Heyden, in Germany)
- selling its stakes (typical in France)
- transforming its power plants to alternative fuel (typical in Germany and in the Netherlands)
- shutdown of its power plant in the frame of capacity auction (typical in Germany)

In Germany it operated seven hard coal and one lignite power plant in 2016 (Uniper, 2016b.) According to the Electricity Market Act, the lignite-fired power plants became a so-called climate reserve. Despite the German government's phasing-out decision on January 29th 2020, the company's plant portfolio was expanded by a new high-efficiency hard coal-fired power plant called Datteln 4, which will remain in operation until 2038 (Uniper, 2020a., 2020b.). According to the act the lignite and hard-coal capacity had to be reduced to 15 GW by the end of 2022, then an additional 6 GW of lignite, 7 GW of hard coal by April 1, 2030, and the rest by 2038. Kiel Power Plant in Germany was decommissioned on March 31, 2019. (Annual Report of Uniper, 2019) Hayden 4 hard-coal-fired power plant with its 875 MW capacity was the first which successfully took part in the German capacity auction. In the second auction the Wilhelmshaven 1 (757 MW) will be home to a green hydrogen plant. This power plant will be transformed into gas-fired, Staudinger 5 (510 MW) by 2025. The Schkopau lignite-fired power plant (900 MW) was sold to Uniper's co-owner, EPH in 2021. (Annual Report of Uniper, 2020) In 2019 the company sold its French interests for risk mitigation purposes. In the United Kingdom, decommissioning (Ratcliffe 2000MW) will take place by 2025. The Dutch government is required to reduce its greenhouse gas emissions by at least 25% by the end of 2020 on the 1990 basis after a lost lawsuit. With this decision, the fate of Dutch coal-fired power plants was also sealed (Uniper, 2020b.) that is why Maasvlakte 3 (1070 MW) will close down by the end of 2029. On the other hand, the compensation awarded is not considered appropriate and is therefore diverted to legal action (Uniper, 2021b.).

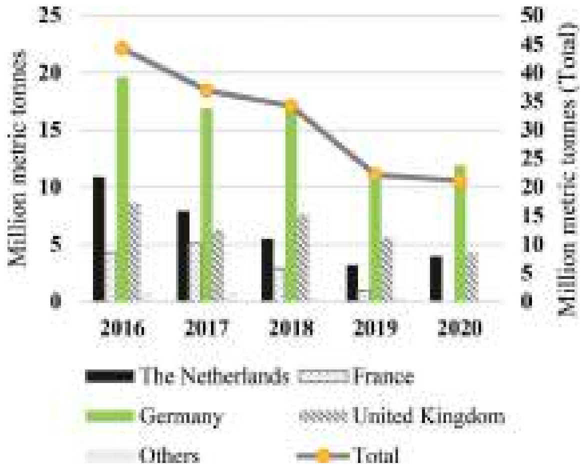

Figure 5. Uniper's direct CO_2 emissions from fuel combustion by country.
Source: Own elaboration based on Uniper's Sustainability Reports 2018-2020

As a result of the former actions and portfolio optimization, the company reduced its CO_2 emission connected to the European Generation by 52 % between 2016 and 2020 (Figure 5).

In 2016 Uniper believed that the coal-based electricity production would increase, but the changed regulation environment did not prove it. On the other hand, the company found a new opportunity in this process, so the adjusted EBIT of the company nearly tripled between 2016 and 2020, and nowadays it develops renewable capacity and invests in clean hydrogen technologies (Annual Reports of Uniper, 2016-2020).

5 CONCLUSIONS

In this article we examined the effects of coal phase-out from the perspective of power plant owners between 2015 and 2020. The extent of the impacts was influenced by a number of factors, such as the composition of the company's portfolio, the share of coal in installed capacity, and the plans to speed up exit from coal-based energy production. Using a case study method we summarised the pathways and strategies of the four most polluter companies operating in the European Union, focusing on their coal phase-out plans. The applied strategies were mostly proactive and similar in the main principles. They wanted to be a leader rather than a sufferer of the transformation. The firms' focus has moved towards renewable energy sources and the diversification of their activities, they invested remarkable amounts in technology innovations. The regulatory environment accelerated the coal phase-out process during the examined period. The ambitious energy and climate policy of the EU and the different regulations of the member states made an increasingly stringent conditions for the power plants. Although coal phase-out severely affected these companies, it did not shake their operation. This may have been due to the fact that the examined period was critical for the conventional electricity generation. Obligation of coal phase-out is put in a different light if the profitability prospects of coal-based electricity generation are considered. The margin of the power generation is influenced by a lot of factors (see Nalbandian-Sugden, 2016; Edis-Bowyer, 2021), such as the development of fuel prices (in this case coal and lignite) as well as the burdens of climate protection efforts (eg. the price of emission allowances, levies and taxes), the declining costs and rapid expansion of renewable energy production as well as the development of wholesale electricity prices. According to several studies (Carbon Tracker, 2018; Edis-Bowyer, 2021) the economic viability of several coal-fired power plants will be questionable in the future and shutdown can be an attractive or even unavoidable option for them. In order to successfully implement the coal phase-out mechanism, it is essential to adhere to the principles of just transition, as well as to ensure the stability of the energy system and supply security. The analyzed annual reports and other sources had been made before energy prices were released in 2021. Compared to the low points in 2020 (largely caused by the Covid-19 epidemic), prices soon reached their pre-epidemic levels. However, the price-boom did not stop. Natural gas prices have risen drastically, 4-6 times in recent months, but electricity prices have also risen significantly, partly due to intense increases in quota prices. There was an upward trend in the price of coal quotations too (Energy Market Report 2021). Analysts say high energy prices will remain in the long run. Next year's reports of the analyzed companies will also provide interesting lessons for dealing with the situation in the energy market.

REFERENCES

Akerboom S. & Botzen W. & Buijze A. & Michels A. & Rijswick M. 2020. Meeting goals of sustainability policy: CO2 emission reduction, cost-effectiveness and societal acceptance. An analysis of the proposal to phase-out coal in the Netherlands. Energy Policy, 138

Annual reports of EPH Group 2015-2020 https://www.epholding.cz/en/annual-reports/

Annual reports of PGE Group 2015-2020 https://www.gkpge.pl/Investor-Relations/financial-data

Annual Reports of RWE 2015-2020 https://www.rwe.com/en/investor-relations/financial-reports-presentations-videos/financial-reports

Annual Reports of Uniper 2016-2020 https://ir.uniper.energy/websites/uniper/English/3000/reporting.html

Bibert S. 2020 H1 Interim Results https://ir.uniper.energy/download/companies/uniperag/Presentations/2020-08 11_H1_2020_Uniper_InvestorPresentation_Final.pdf

Brauers H. & Pao-Yu O. 2020. The political economy of coal in Poland: Drivers and barriers for a shift away from fossil fuels. Energy Policy, Volume 144, ISSN 0301-4215.

Brauers H. & Pao-Yu O. & Walk P. 2020. Comparing coal phase-out pathways: The United Kingdom's and Germany's diverging transitions. Environmental Innovation and Societal Transitions, Volume 37, Pages 238–253, ISSN 2210-4224.

Carbon Tracker 2018. Powering Down Coal: Navigating the economic and financial risks in the last years of coal power. https://carbontracker.org/reports/coal-portal/

Chestney N. 2020 Nearly half of global coal plants will be unprofitable this year: Carbon Tracker. Reuters, 8. April. 2020

Edis T. & Bowyer K. T. 2021. Fast Erosion of Coal Plant Profits in the National Electricity Market, IEEFA

Energy Market Report 2021: Energiapiaci összefoglaló 2021/18. Energymarket24 Kft. https://energymarket24.hu/

ENSZ 2020. Fenntartható fejlődés energetikai vonatkozásai https://www.un.org/sustainabledevelopment/energy/

Europe Beyond Coal, 2021a: Overview: National coal phase-out announcements in Europe https://beyond-coal.eu/wp-content/uploads/2021/08/Overview-of-national-coal-phase-out-announcements-Europe-Beyond-Coal-3-August-2021.docx.pdf

Europe Beyond Coal, 2021b: European Coal Plant Database https://beyond-coal.eu/database/

Eurostat 2021: CO2 emissions from energy use clearly decreased in the EU in 2020, 07/05/2021 https://ec.europa.eu/eurostat/web/products-eurostat-news/-/ddn-20210507-1

Gillich A. & Hufendiek K. & Klempp N. 2020. Extended policy mix in the power sector: How a coal phase-out redistributes costs and profits among power plants. Energy Policy, Volume 147, ISSN 0301-4215

Global Energy Monitor 2021. https://globalenergymonitor.org/projects/global-coal-plant-tracker/summary-data/

Heinisch K. & Holtemöller O. & Schult C. 2021. Power generation and structural change: Quantifying economic effects of the coal phase-out in Germany. Energy Economics, Volume 95, ISSN 0140-9883.

Heinrichs H.U. & Markewitz P. 2017. Long-term impacts of a coal-phase out in Germany as part of a greenhouse gas mitigation strategy. Appl. Energy, 192, pp. 234–246,

IEA 2021. Electricity Market Report July https://iea.blob.core.windows.net/assets/01e1e998-8611-45d7-acab-5564bc22575a/ElectricityMarketReportJuly2021.pdf

International Trade Administration 2021 Energy sector of Poland https://www.trade.gov/country-commercial-guides/poland-energy-sector

IRENA 2017: REthinking Energy 2017: Accelerating the global energy transformation https://www.irena.org/publications/2017/Jan/REthinking-Energy-2017-Accelerating-the-global-energy-transformation

Keles D. & Yilmaz H. Ü. 2020. Decarbonisation through coal phase-out in Germany and Europe — Impact on Emissions, electricity prices and power production. Energy Policy, Volume 141, ISSN 0301–4215.

Lund, P.D. 2017. Implications of Finland's plan to ban coal and cutting oil use. Energy Policy, 108 pp.78–80

Markard J. & Rinscheid A. & Widdel L. 2021. Analyzing transitions through the lens of discourse networks: Coal phase-out in Germany. Environmental Innovation and Societal Transitions, Volume 40, Pages 315–331, ISSN 2210-4224.

Maubach K. & Tuomela T. 2021a, b: 3M 2021 Interim Results Interim Results presentation Uniper-presentation https://ir.uniper.energy/download/companies/uniperag/Presentations/20210506_Q12021_UniperInvestorPresentationF.pdf

Maubach K. & Tuomela T. 2021b,c: H1 2021 Interim Results presentation Uniper-presentation https://ir.uniper.energy/download/companies/uniperag/Presentations/2021-08 11_H1_2021_Uniper_Investor_Presentation_Final.pdf

Nalbandian-Sugden H. 2016. Operating ratio and cost of coal power generation, IEA Clean Coal Centre

Osorio S. & Pietzcker R. C. & Pahle M. & Edenhofer O. 2020. How to deal with the risks of phasing out coal in Germany, Energy Economics, Volume 87, ISSN 0140-9883.

PGE groups strategy 2020. https://www.gkpge.pl/investor-relations/PGE-Group/pge-group-s-strategy

Rentier G. & Lelieveldt H. & Kramer G. J. 2019. Varieties of coal-fired power phase-out across Europe. Energy Policy, 132, pp. 620–632,

Ron Chan H. & Fell H. & Lange I. & Li S. 2017 Efficiency and environmental impacts of electricity restructuring on coal-fired power plants. Journal of Environmental Economics and Management, Volume 81, Pages 1–18, ISSN 0095-0696

Sustainability Reports of Uniper 2016-2020 https://ir.uniper.energy/websites/uniper/English/3000/reporting.html

UNFCCC 2021: The Paris Agreement https://unfccc.int/process-and-meetings/the-paris-agreement/the-paris-agreement

Uniper 2016a. Sustainability Report 2016 Short version https://ir.uniper.energy/download/companies/uniperag/Sustainability/Uniper_SR16_short.pdf

Uniper 2016b.: Lists of Assets https://ir.uniper.energy/websites/uniper/English/3000/reporting.html

Uniper 2020a.: Uniper strategy highlights Andreas Schierenbeck, CEO Uniper Fortum Capital Market Day, December 3, 2020 https://ir.uniper.energy/download/companies/uniperag/Presentations/2020-12-03_Uniper_Strategy_Schierenbeck.pdf

Uniper 2020b: Quarterly Statement Q1-Q3 Financial Result https://ir.uniper.energy/download/companies/uniperag/Quarterly%20Reports/DE000UNSE018-Q3-2020-EQ-E-00.pdf

Uniper 2021a.: Fact Sheet https://irpages2.eqs.com/download/companies/uniperag/factsheet_17739_English.pdf

Uniper 2021b. Half Year Interim Report 2021, Financial Results https://ir.uniper.energy/download/companies/uniperag/Quarterly%20Reports/DE000UNSE018-Q2-2021-EQ-E-00.pdf

Van den Bergh J.C.J.M & Botzen W.J.W. 2015. Monetary valuation of the social cost of greenhouse gas emissions. Ecological Economics, 114, pp. 33–46.

Entrepreneurship in the Raw Materials Sector – Bartha et al. (Eds)

Spent pickling liquor as industrial waste recover opportunities

H. Zakiyya & T. Kékesi
Faculty of Material Science and Engineering, University of Miskolc, Hungary

ABSTRACT: Pickling is one of the essential steps in galvanizing industries in which hydrochloric acid (HCl) is used as the main composition to clean up the steel surface. This HCl lost its pickling efficiency because of decreasing in its concentration as well as increasing metals content because of dissolution processes. Recovery processes could be done to this kind of waste, so circular economics and a nearly zero waste cycle industry can be established. Processing SPL by electrodeposition is possible to recover pure metal from the waste solution. However, the presence of iron in the zinc chloride solution changes the nature and the conditions. It was found that the effect of iron concentration on the polarization curves is complex. Initially it has a negative effect on the generated cathodic current because of the enhancement of hydrogen bubble formation. Further increased iron concentrations may make the composition of the Zn-Fe deposit dominantly in favour of iron, resulting in a hydrogen dominated cathodic mechanism. Controlling the parameters such as Zn and Fe concentration, and the electrolyte's agitation intensity could play essential impacts on the electrodeposition of zinc from chloride media. Nevertheless, separation is still essential; thus, introducing the anion exchange separation to prepare the electrolyte is needed to achieve an acceptable quality of zinc deposition. In the relatively low concentration of HCl, Zn tend to be retained in the resin as its more likely to produce chloro-complex. As in the higher concentration of HCl (>1), Fe-(III) distribution fucntion in HCl will increase thus the Fe may retain in the resin. However oxidation state control can be the answer of this problem by reducing Fe(III) to Fe(II) or in order to optimalize the separation process partially precipitation of Fe might be an option.

Keywords: *Spent Pickling Liquor (SPL)*, *Zn-Fe recovery*, *liquid waste*, *electrowinning*

1 INTRODUCTION

Preventing corrosion on the surface of metals is one of the necessary steps in the metal production. One of the most common corrosion control methods is coating the surface by a passivating layer, like in the case of hot dip galvanizing, where the surface of the steel object is protected by a zinc layer. This process consists of subsequent steps, where pickling is an important for preparing the surface (Agrawal et al. 2009; Regel-Rosocka. 2010; Csicsovszki et al. 2005). In this step, some acids, namely hydro chloric (HCl) or sulfuric (H_2SO_4) acids are applied to remove the oxide layer (Abad et al. 2017; Regel-Rosocka et al. 2010). In practice, quite a large proportion of the products with faulty zinc coatings are returned to this step, which results in the enrichment of the pickling liquor in also zinc, beside iron, and the acid concentration decreases at the same time. At a level of 15 – 30 % of the original acid concentration, the solution is categorized as spent, i.e. no longer serviceable, while the metal content, primarily Zn (II) and Fe (II) is increased to 150-250 g/dm^3 (Regel-Rosocka 2010). In this condition, the rate of oxide dissolution by acid is getting slower. Sonmez et al. 2003 has found

DOI: 10.1201/9781003259954-17

that the zinc concentration of the solution increased faster than that of iron when H_2SO_4 was used. Due to the heavy metal content, spent pickling liquor (SPL) is categorized as a hazardous waste, and need to be treated before disposal.

An ideal treatment of this liquor can be not only satisfactory for the environment but can also serve the economy by recovering valuable metals, Zn and/or Fe in this case. Due to environmental protection regulation, the processes of Zn recovery from various industrial wastes are lately becoming progressively more attractive. If the metals can be extracted at a high purity level, the processing of the waste material may offer some extra economic benefit (Kekesi et al. 2002). The price of zinc, as of all the metals, strongly depend on purity. For example, the 99.999% (5N) purity zinc (available as a special material) may cost almost 4000 times more than the common commodity at the metal markets. Therefore, treating such waste materials may become more promising if the recovery process is capable of reaching higher purities. This is one of the goals of the envisaged research challenge.

1.1 *Spent Pickling Liquor (SPL) treatment*

It has been reported by European stainless steel and alloyed steel companies that approximately 300 000 m^3 of spent pickling liquor is produced every year. This stream is neutralized to produce 150 000 t/y of sludge, which is stored (Frias et al. 1997). Neutralization with an alkaline agent is widely used in spent pickling liquor treatment due to its simple and economical procedure to treat relatively dilute low-cost heavy metal solutions. According to the restriction by the Environmental Protection Agency (EPA) for steel pickling plants, the HCl limit in the air is 6 ppm for continuous and 18 ppm for batch processes. Also, the European standards state that the metal and chloride ion contents after neutralization must not be higher than 2 mg/dm^3 Zn, 10 mg/dm^3 Fe and 1 g/ dm^3 Cl^- with the acidity range between 6 and 9. Thus the effluent has to be treated to meet these regulations and to prevent environmental pollution.

The properties of the neutralization product depend on the composition of the SPL, which varies according to the plant of origin. Table 1 is one of the example of SPL composition, a wider survey (Regel-Rosocka. 2010b) suggests the following characteristic ranges of composition for the SPL obtained from pickling applied before hot dip galvanization: 30 ~ 80 g/dm^3 Zn, 50 ~ 150 g/dm^3 Fe and 40 ~ 160 g/dm^3 HCl. However, the Zn content greatly depends on how the recycled products are treated. If removal of the faulty zinc layer is carried out separately, stripping solution of higher Zn concentration also arises. In other cases, the SPL carries the whole of the stripped zinc.

Table 1. Chemical composition of hot-dip galvanizing waste.

Waste	Process	Phase	Chemical composition	
Spent Pickling Liquor (Sonmez et al. 2003)	Pre-treatment (Pickling)	liquid	Cu	0.56 mg/dm^3
			Co	1.99 mg/dm^3
			Ni	10.70 mg/dm^3
			Pb	18.68 mg/dm^3
			Cd	1.36 mg/dm^3
			Cr	3.07 mg/dm^3
			Mn	230 mg/dm^3
			Cl (total)	185 g/dm^3
			Fe^{2+}	45.83 g/dm^3
			Fe^{3+}	6.49 g/dm^3
			Fe (total)	52.32 g/dm^3
			Zn	95.45 g/dm^3
Stripping Liquor (Hluchanova et al. 2012)	Special pre-treatment	liquid	Zn	97 %

Beside the main components – zinc and iron (with the predominance of the Fe(II) form) – the spent solution left over from hot-dip galvanizing contains also a little amount of lead, chromium and some other metals together with hydrochloric acid. The concentration ranges from plant to plant relatively wide, which makes it difficult to use a universal method. The regeneration of the pickling liquor is the first idea coming up to minimize the pollution and to reduce the costs incurred by the fresh acid requirement.

Some recycling processes have been developed to turn spent pickling liquors into valuable secondary resource but the process to generate both acid and metal in an economical and practical way, still needs further research. The main problem is the physico-chemical complexity of transition metal ions in hydrochloric acid effluents (Regel-Rosocka 2010). Consequently, it is difficult to choose the proper method to be used. Nowadays, a number of technologies such as precipitation, membrane separation, ion exchange, electrowinning, pyrohydrolysis, liquid-liquid extraction, diffusion dialysis, hydrolysis, solvent extraction and oxidation are combined to get a better results (San Román et al. 2012). Table 2 describes the advantages and disadvantages of various traditional technologies in SPL regeneration.

Table 2. Various technologies of SPL treatment (Regel-Rosocka. 2010b).

Technology	Efficiency	Advantage	Disadvantage
Spray roasting		Effective for large amount	Limited by Zn concentration
		Reduce wastewater and sludge	High operating cost
		Cost covered by the result	Complex installation
		Applied	High NO_x release
Precipitation/ Neutralization		Low operating cost	Large consumption of chemical
		Neutral by-product	No acid recovery
		Simple technique and equipment	Expensive sludge storage
		Can be applied in the small industry	Hazardous precipitate High nitrogen content
Retardation/ ion-exchange	Recovery of metal salt 50-55%	Effective Zn retention	Limited metal ion concentration
		Effective selectivity	High volume of waste
		Low operation cost	High volume of diluted solution
		Little equipment and space	High consumption of fresh water
		Applied in industry	
Solvent Extraction Solvent Extraction	91 % of extraction Fe 91 % of extraction Fe	TBP is effective for wide range of Zn concentration in feed	Organic impurities in aqueous phase
		Good selectivity with TBP	Extractant loss
		Acidic extractant permit Zn up to 100 g/dm^3 after stripping	Stripping problem from certain extractant
		High production with compact equipment	Co-extraction of Fe(III) with Zn Phase separation after stripping
			The greater the feed concentration the higher treatment cost

Membrane technologies combined with electrowinning is one of the promising directions of research where Zn(II) ion can be separated from Fe(II) before further recovery of either of these two metals. Separation is performed to prevent the contamination of one recovered metal by the other ion in electrowinning. It has to be carried out also because hydrolysis of a metal may locally disturb the conditions of the electrodeposition of even the more noble metals (Díaz et al. 2002).

1.2 *Electrowinning of zinc from SPL and its challenges*

The application of electrowinning is possible by depleting metal from the solution through cathodic deposition. Electrochemical separation of various metals in the solution can be done due to relative potential differences. Through electrochemical processes metal ions in HCl solutions are electrodeposited to the cathode of an electrolytic compartment. This technique is believed to be economically friendly. In hydrometallurgy, electrodeposition is often applied together with other predominant techniques of solution purification, such as membrane separation, ion exchange and solvent extraction. As a result, this technique offers pure metal and acid regeneration form SPL.

Zinc recovery from SPL through zinc electrodeposition still faces some challenges, one of which is the energy consumption due to the competition between zinc and hydrogen ions at the electrolyte/electrode interface. As reported in many studies, zinc deposition is often coupled with the evolution of hydrogen. Due to the readily formed zinc-chloro-complex species (Kekesi 2018; Kekesi et al. 2002), the metal deposition must be preceded by the dissociation of the complex structure, liberating the electro-active cation:

$$[\mathrm{ZnCl}_x]^{(2-x)-} = \mathrm{Zn}^{2+} + x\mathrm{Cl}^- \tag{1a}$$

$$\mathrm{Zn}^{2+} + 2e^- = \mathrm{Zn} \tag{1b}$$

This mechanism has a natural inhibiting effect at the cathode, but also some bubbles are produced by hydrogen evolution at the same time:

$$2\mathrm{H}^+ + 2e^- = \mathrm{H}_2 \tag{2}$$

The complex form of the dissolved zinc even in weak HCl solutions may be a reason why the ion supply to the cathode surface is hindered. This case has also been found with tin in HCl media (Kulcsar et al. 2016). However, the inhibiting effect of the preliminary complex dissociation may have a beneficial effect on the structure of the formed cathodic deposit.

Besides the types of crystal growth, another challenge in zinc electrodeposition from a Zn-Fe mixed chloride solution is the interference of the main cathodic process caused by the side-reactions with the iron species. The redox potentials of the Fe^{2+}/Fe and the Fe^{3+}/Fe^{2+} couples are -0,44 and +0,74 V, respectively (Kekesi. 2018). These potentials directly indicate the stability of the Fe^{2+} oxidation state if metallic iron is present in the system and oxidation by as strong agent (like oxygen in the ambient air) can be excluded. Zinc, with its more negative standard electrode potential of the Zn^{2+}/Zn couple, will also directly reduce the Fe(III) species, if present. However, the oxidation by air or also by the anode can always generate the ferric species, which – coming in contact with the deposited metal – may cause cathode corrosion:

$$2\mathrm{Fe}^{3+} + \mathrm{Zn} = \mathrm{Zn}^{2+} + 2\mathrm{Fe}^{2+} \tag{3}$$

$$\mathrm{Fe}^{3+} + \mathrm{Fe} = 2\mathrm{Fe}^{2+} \tag{4}$$

Although, the formation of the respective chloro-complex species:

$$\mathrm{Me}^{z+}{+}x\mathrm{Cl}- =[\mathrm{MeCl}x]^{z-x} \tag{5}$$

may influence the Me(Z)/Me formal potentials, where *z* is the charge of the aquo-ions, Z is the valence of the oxidation state and *x* is the coordination number of the chloride ions in the complex species formed (Csicsovszki et al. 2005; Kekesi. 2018). As the concentration of HCl is limited to a low level by keeping the pH in the electrolyte preferably above the 2-3 value, the formation of the complex species will depend only on the free Cl^- ions dissociated from the added chloride salts used in preparing the tested synthetic electrolytes. There may also be a difficulty in terms of energy consumption because of the competition between zinc and hydrogen ions at the electrolyte/electrode interface. Zinc deposition is expected as the dominant cathodic reaction. However, Fe impurity content in the electrolyte may promote also the hydrogen ion reduction, because the overpotential of hydrogen on iron is lower (by ~ 400 mV) than on zinc(Kekesi. 2018).

Anion exchange, offers a clean separation of iron in the Fe(II) state from zinc. Figure 1 shows the known and relevant anion-exchange distribution functions, which can be used for devising the separation procedure.

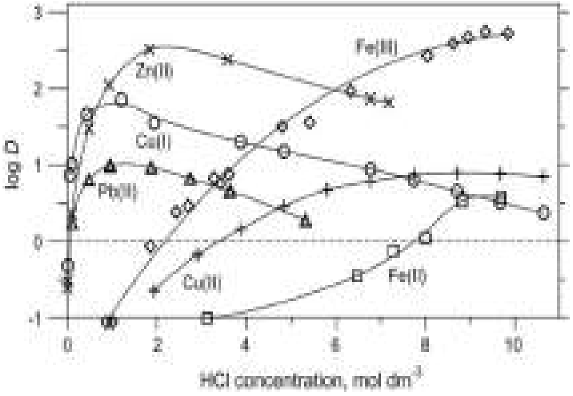

Figure 1. Anion exchange distribution functions of Zn and Fe (a) and those of the Sn species (b) determined by batch equilibration. (Kekesi et al. 2002).

The most important task is the elimination of iron, separation of iron requires a preliminary reduction of the trivalent species according to Eq. (4) by stirring iron chips in the mixed solution of the SPL. We have performed this step in the laboratory, and the efficiency was found satisfactory within several minutes. The solution was not re-oxidized if kept still in a closed container within any appreciable time. Feeding the original SPL into the anion-exchange column, Fe(II) is directly eliminated in the first effluent, containing the original concentration of HCl too, while zinc is fixed in the resin bed. Elution of the purified zinc is possible by a low concentration (1 0.01 – 0.05 M) HCl, just to prevent any hydrolytic precipitation. If separation of tin is also required, the zinc elution process needs to be further refined.

Separation of metals as dissolved ions in the solution by anion-exchange can be extremely efficient if the tendencies of chloro-complex formations are appreciably different for the metals in question. The resin may contain mobile counter-ions (A^- anions) worked as the exchanger for corresponding anionic complex ions of the metals in solution (Kékesi. 2002; Kekesi et al. 2003). This separation can be carried out by adjusting the chemical properties of the aqueous solution, i.e. the concentration of the complexing ions, to match the favorable condition of either sorption or elution in contact with the strongly basic anion exchange resin. The purification of the solution can be done through feeding the appropriate eluent to either bacth or vertical column containing anion-exchange resin at controlled rate. If the distribution coefficients are largely different, as in the case of Zn(II) and Fe(II), the separation can be executed also by a batch procedure where the two phases are simply mixed for a certain time and then separated. Chromatographic separation, however, in a vertical bed of the resin in a column (of a length of approx.. 10 times tits diameter) may offer separation of species showing less difference in their distribution coefficients.

In view of the possibilities related to investigate the best method to recycle the liquid waste of hot-dip galvanizing, the spent pickling liquor (SPL), our main purpose is to determine the conditions and the suitable processes of an efficient zinc extraction procedure offering a pure metallic product, while allowing the residual liquor to be used for regenerating the HCl content too. Thus the waste could be transformed into a valuable resource.

1.3 *High-value materials prepared from SPL*

There are various metal ions in SPL which can be considered as a resource of high value materials such as ultra high purity iron or iron oxides, high purity zinc or zinc salts. Another prospective product is ultra high purity iron that is also promising commercial product for semiconductor grade silicon, it was proved by Kekesi et al (Kekesi et al. 2002), that a two-step anion exchange technology – combined with the redox conditioning of the chloride solution of proper HCl concentration - is suitable to eliminate the other metal ion contamination. Iron yields over 80% could be reached by optimizing the anion-exchange procedure controlling the oxidation states and the degrees of chloro-complexation of the ionic species to be separated under optimum condition (Kekesi et al. 2002). Further, it may significantly increase the value of SPL by producing nano-sized iron oxide powder which has wide range application on magnetic recording material and biological technology (Tang et al. 2016).It may be related to the preliminary solution purification step if the cathodic deposition of pure zinc is the main objective. The value of these products may overwhelm the economical advantage of eliminating the costs of incurred by the otherwise mandatory treatment and handling of the hazardous material.

2 MATERIAL AND METHOD

In this preliminary research two main processes were carried out to confirm the possibility of producing pure Zn from SPL by combining electrowinning and anion exchange. Electrodeposition is the essential technique to recover Zn from the SPL. The preliminary separation process to purify the SPL is a necessary part of the scheme, as pure zinc cannot be obtained from a solution heavily contaminated by iron. Therefore, solution purification by anion-exchange in this case, has to be included. In all the experiments so far, model solutions prepared from reagent grade chemicals have been applied. The potentiodynamic experiments to characterize Zn deposition from SPLwere performed with 85 cm^3 volume of the solutions. The initial cathode was made of copper plate with the active surface of 2 cm^2 and the anode was made of a pure zinc rood of 5 mm diameter. The cathode surface was polished with an 800 grit SiC paper giving a uniform surface, then washed with distilled water and acetone, finally dried before setting into the cell. All the runs were carried out at room temperature with 40 mV/s continuous polarization speed – giving the widest range of clear results - and with 10/s sampling rate. The composition of the Zinc deposit was determined by Atomic Absorption Spectrophotometry (AAS) using zinc hollow cathode lamp at 213.9 nm wavelength. While the iron determination were did by ratio of weight of total deposits.

3 RESULT AND DISCUSSION

In the first series of the experiments, our aim was to identify the dominant cathodic process in different ranges of the examined parameters. Zn deposition was investigated from pure "synthetic" Zn chloride solutions by the potentiodynamic technique, applying a specially developed potentiostat that could follow the rapidly changing surface conditions by increasing the current in the required pace. The deposits were observed to form irregular growths of dendrites and loose crystals as can be seen in the Figure 2.

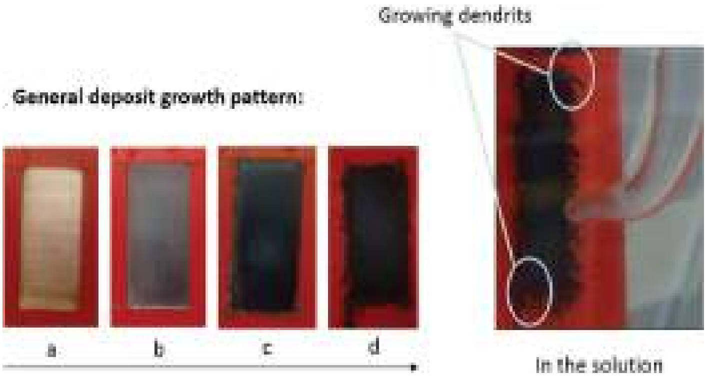

Figure 2. The changes of the cathode surfaces during potentiodynamic polarization start with (a) Cu starting surface, (b) uniform densed deposition, (c) black spongy deposit and (d) dendritic deposition. (1 min runs at 40 mV/s polarization speed).

Acceptable deposition of Zn on the cathode mainly depends on the composition of the bath, in which various agents may influence the deposition process and the structure of the final deposit. Chloride solutions offer higher rates of zinc deposition on the cathode surface compared to that of sulphate systems. However, it is hard to obtain smooth and compact deposits. From the result it seems that deposit tend to be fine-grained at the initial phase where the current relatively observed low and the active surface relatively constant, as more deposit colected on the surface of the cathode the more active cathode was developed and the deposit more likely to be sponge-like and dendritic. Besides the evolution of hydrogen obtained along with metal deposition also effect the morphology of the deposit. So the hydrogen ion concentration in the chloride solution has to be controlled.

In correlation with the visual observations. It is observed that the generated current tends to be decreased by increasing iron concentration in the 0 – 45 g dm^{-3} range. This infers a lower deposition rate as more iron is in the solution (Figure 3). However, if the iron concentration was increased further to 60 g dm^{-3}, the tendency changed and the current increased. As the iron concentration got high enough, hydrogen evolution dropped in favour of metal deposition and the surface was less blocked by initiated gas bubbles, thus also enhancing zinc deposition. The latter

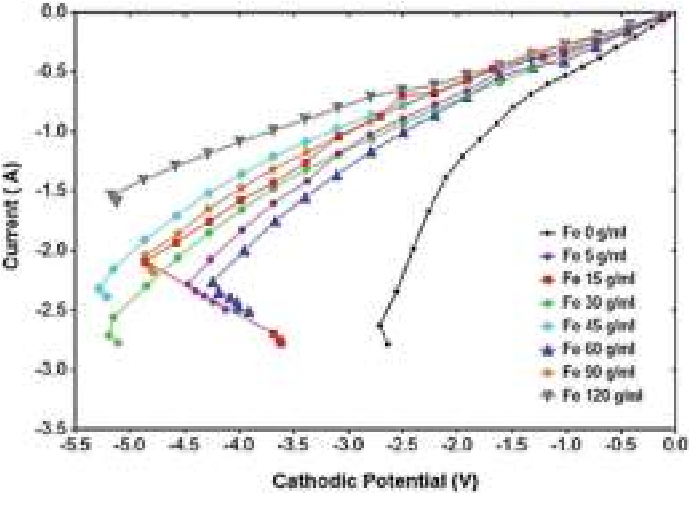

Figure 3. Cathodic polarization curves at different Fe concentrations (0 r.p.m.) (1 min runs at 40 mV/s polarization speed).

is characterised by a stronger dendrite formation. Further increasing the iron concentration, as far as 120 g dm^{-3}, however resulted in the overwhelming dominance of iron deposition. It mostly produces powdery deposits, and the iron particles are easily detached, therefore the picture shows smoother surfaces, but the solution becomes turbid with the dark iron powder mixed in. The backdrop potentials were also shifted to more negative values, confirming that less metal could be deposited at the lower ranges of polarization without agitation because of hydrogen blocking. It also proves that iron in the solution promotes hydrogen evolution at the cathode.

Another remarkable difference is found in the changing of the slopes during polarization. In the case of the pure zinc solution and also if the added iron concentration was very low, the slope of the curve could get much steeper as the cathodic polarization was increased. This reflects a stronger formation of dendrites, i.e. a faster growth of the actual surface. However, if iron is added at higher proportions to the solution, the slope virtually remains constant, although the Buttler-Volmer-Erdey relationship (Kekesi. 2018) suggests that with constant surfaces the curve should be exponential. This discrepancy can be explained by the blocking effect of the evolved hydrogen bubbles adhering for some considerable time to the cathode surface. Thus the more constant the slope of the polarization curve is the more dominant the hydrogen reduction can be. It can be seen in the case of the highest concentrations of iron in the electrolyte.

A further difference in the shapes of the polarization curves may be expressed by the observed voltage ranges and the finally occurring potential backdrop forming a virtual hook. As the potentiostat is capable of supplying a total voltage of only 10 V, the conditions may also be limited at the end of the polarization runs by the voltage drop required to drive the current through the main cell from the counter electrode (anode) to the work electrode (cathode). If the polarization curve can span only a short potential range, the resistivity of the complete electric circuit may be high. With the applied constant anode-cathode distance, it is also a good indication of the resistivity of the solution. In the case of iron addition, the hydrolytic conditions expressed by the following reaction

$$FeCl_3 + 3/2H_2O = Fe(OH)_3 + 3HCl \tag{4}$$

resulted in a more acidic solution (pH 1 ~ 1.3), which allowed the relative potential of the cathode to develop further. In the case of the pure zinc solution, on the other hand, the actual surface of the cathode was quickly change for a larger area by the effectively developed dendrites requiring less polarization potentials, but the whole electric circuit reached the maximum voltage supplied by the instrument as the solution was closer to the neutral state (pH 4 ~ 5). This is an obvious reason why iron addition to the $ZnCl_2$ electrolyte solution was found to enhance hydrogen evolution during cathodic polarization.

Comparing the final deposits obtained in the equally 1 min long polarization runs, it is evident, that the masses are different. Figure 4 demonstrates this effect on the metal deposition

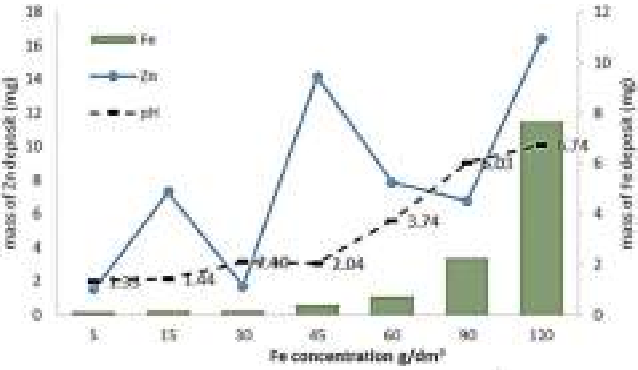

Figure 4. Deposit composition obtained from solutions of 90 g/dm^3 Zn with various concentrations of Fe.

from the mixed electrolytes, which requires more experimentation for its elucidation. Therefore, polarization experiments were carried out in the same mixed solutions with copper substrates as starting cathodes of carefully measured masses.

The highest mass of zinc in the deposit was obtained in the range of 45 to 60 g/dm^3 Fe in the solution. The acceleration of Zn electrodeposition by the Fe content of the solution is also shown by the results in Figure 4. In these experiments the obtained and dried deposit was weighed, followed by a complete dissolution in 1 M HCl from the copper substrate, and finally the iron mass was calculated from the analyzed concentration. The deposited mass of zinc was determined by subtracting the iron mass from the total mass of the deposit.

The columns in Figure 4 show that the amount of iron deposited from the mixed solution is increasing quickly as the Fe concentration is increased beyond 30 g/dm^3. However, zinc deposition is also increased concomitantly. It is also seen that the intensity of stirring has a strong effect on the rate of zinc deposition. It can be also seen for iron in the 45 – 90 g/dm^3 Fe concentration range of the mixed solutions. At the highest iron concentration, however, stirring seems to lose its relative importance. Comparing the positions of the curves (indicating the Zn deposit) and the bars (standing for the Fe deposits), it is seen that from stirred solutions of 90 g/dm^3 Zn and various Fe concentrations the purest Zn deposit can be obtained at the lowest iron concentrations. If however, the solution is stationary, and there is little iron in it, the deposit was too small in mass to make accurate measurements.

With increasing contamination of Fe in the electrolyte solution, hydrogen evolution will increase because of its lower overpotential to Fe. The generated gas bubbles give an extra stirring at the surface of the cathode, enhancing the transport of the zinc ions. It may increase the rate of Zn deposition as seen in the 30 – 60 g/dm^3 range of iron concentration. With even more iron in the electrolyte, the mechanical effect of hydrogen evolution is outweighed by the chemical effect of strongly increasing local pH. It may trigger a local formation of hydroxide particles. Thus an inhibiting layer can be formed hindering the deposition of the less noble zinc. Therefore, in the 30 – 60 g/dm^3 Fe range, where Zn deposition is enhanced, the increased rate of iron deposition results in more contaminated zinc deposits. This is especially true if the solution is not stirred intensively. At higher iron concentrations, even more contaminated zinc deposits can be obtained. Therefore, in order to obtain pure zinc from the SPL, it is necessary to apply the planned preliminary purification of the solution, removing iron as much as possible.

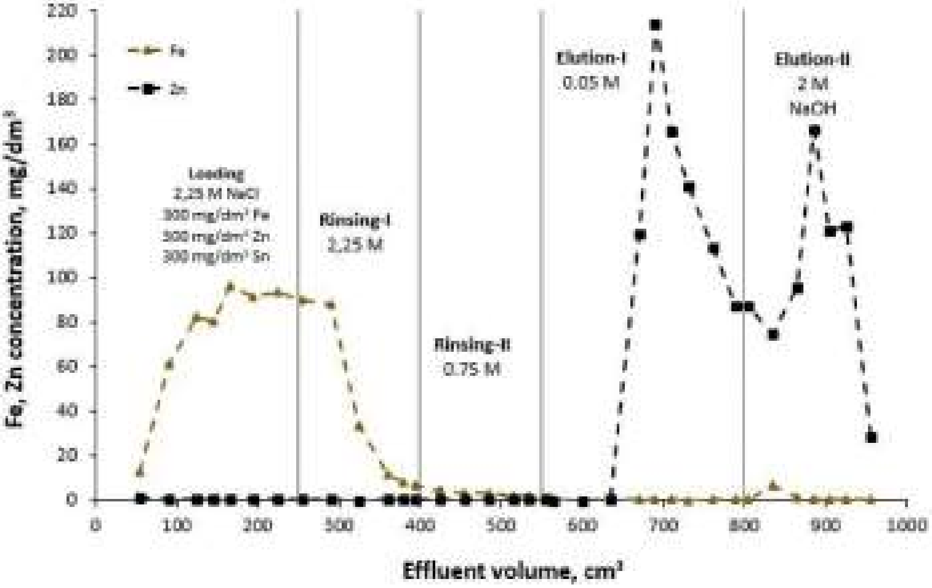

Figure 5. Elution curves of the preliminary anion exchange purification.

Anion exchange is one of the best technique as suggested in former experimental results (Kékesi 2002; Kekesi et al. 2003;Uchikoshi et al. 2004) if high purity is aimed. In the case of SPL, the anion exchange method not only offers a perfect separation of the impurities but also helps in regenerating the acid in a further process. The first effluent will contain almost the whole HCl loaded with iron (and some minor impurities of Ni, Co or Mn) as the metallic content. This solution can be evaporated to regain the pure HCl and the residue can be processed to obtain the metals in either metallic or compound form. The results of the devised procedure can be seen in the elution diagram of Figure 5. The devised anion exchange procedure could selectively remove Fe from the solution, mostly during the loading step. The removal of iron is continued as the mobile phase in the resin bed is replaced by a pure NaCl solution of the same concentration. Rinsing was continued with 0,75 M HCl just to see if any Fe(III) could be present mostly depressed to the bottom of the resin bed, and to remove any incidentally precipitated iron hydroxide. It proved that the initial reduction of iron to the Fe(II) state by stirring the solution with iron chips was virtually complete. Reducing the chloride ion concentration to 0.05 mol/dm^3 could initiate a sharp peak of zinc elution.

In this case, HCl was used to prepare the eluent, so as not to risk any precipitation of zinc in the resin bed. This step also removed some tin, which must have been present in the divalent form. it may be just negligible in real SPL solutions, but a second anion-exchange step under oxidizing conditions could eliminate also this minor leakage. The recovery of zinc by the 0.05 M HCl elution may not have been complete, but applying a longer elution with this eluent and somewhat slower flow rate could improve it in practice. Another way to improve the recovery feature in the elution step can be a moderate decrease in the applied HCl concentration as far as e.g. 0.01 M HCl. The residual zinc was finally removed by applying 2 M NaOH in a secondary elution step.

3.1 *Benefits of the process*

Every year, 300 000 m^3 of discarded pickle liquor are produced in Europe, leading in costly and energy-intensive handling, treatment, and disposal. The offered technology solves the problem of waste disposal, resulting in significant savings in operating, environmental, and capital expenditures. As well as the costs of manufacturing hydrochloric acid to replace the spent liquor solution. The benefits of the purposed method are decribed as follow:

- Domestic energy savings of about millions barrels of crude oil equivalent per year compared to the present process by replacing the roasting method of regenerating SPL
  - For 800 m^3 per day SPL, this new process offers saving of ~ 870 billion Btu per year of processing energy.
  - saving transport energy as well as the CO_2 cost.
- Annual cost savings in by avoiding the need to neutralize and bury waste pickling liquor in landfills.
- Raw material saving cost for HCl regeneration
- Eliminates the need to bury neutralized pickling waste, which has significant environmental benefits.
- Creates a marketable and valuable product by on-site service

4 CONCLUSION

Regarding to six categories of BAT requirement, such as: (i) implementation in industry, (ii) energy saving, (iii) low emission of green-house gases, (iv) reduced use of fresh chemicals and water, (v) reduction of waste streams, and (vi) recycling of chemicals, the purposed technology can meet the requirements. In the case of electrowinning, a successful iron deposition has already been reported by former research activities at the University of Miskolc. However, in the current SPL from Hungarian hot dip galvanizing plants, and the implied economical potential justify the consideration of a reversed approach where the recovery of pure zinc is targeted in the first place. Recovery of pure Zn from SPL solution can be done by electrodeposition process but the contamination of other elements in the solution, especially Fe, decreasing the efficiency of the process. As a result, in order to acquire pure zinc from the SPL, the solution must undergo the specified preliminary purification, removing as much iron as feasible. Anion exchange separation can perfectly remove iron in the Fe(II) state. As the testing of the devised procedure proved, relatively low concentration of chloride ions, naturally present in the treated solution form anionic chloro-complex species of zinc, thus it is strongly fixed in the resin bed of strongly basic anion-exchange resin in the chloride form.

With the new method, the cost of waste processing is eliminated, as is the cost for purchasing raw materilas of the fresh pickling reagent. By-product sales of pure metals (Zn) used for industrial need are an additional economic benefit of the novel technique. However, further investigation is required to develop a better understanding of the whole process.

REFERENCES

Agrawal, Archana. et al. 2009. “An Overview of the Recovery of Acid from Spent Acidic Solutions from Steel and Electroplating Industries.” *Journal of Hazardous Materials* 171 (1–3): 61–75. https://doi.org/10.1016/j.jhazmat.2009.06.099.

Carrillo-Abad, J. et al. 2017. “PH Effect on Zinc Recovery from the Spent Pickling Baths of Hot Dip Galvanizing Industries.” *Separation and Purification Technology* 177: 21–28. https://doi.org/10.1016/j.seppur.2016.12.034.

Csicsovszki et al. 2005. “Electrodeposition of Iron from Spent Hydrochloric Pickling Solutions Containing Fe(II) and Zn(II).” *Unpublished Manuscript, University of Miskolc*.

Csicsovszki, Gabor. et al. 2005. “Selective Recovery of Zn and Fe from Spent Pickling Solutions by the Combination of Anion Exchange and Membrane Electrowinning Techniques.” *Hydrometallurgy* 77 (1–2): 19–28. https://doi.org/10.1016/j.hydromet.2004.10.020.

Díaz, S. L. et al. 2002. “ZnFe Anomalous Electrodeposition: Stationaries and Local PH Measurements.” *Electrochimica Acta* 47 (25): 4091–4100. https://doi.org/10.1016/S0013-4686(02)00416-4.

Frias, Carlos. et al. 1997. “Novel Process to Recover By-Products from the Pickling Baths of Stainless Steel.” Project Funded by the European Community under the Industrial & Material Technologies Programme (Brite-Euram III), Project BE-3501, Contract BRPR-CT 97-0407, 1997–2000. 1997. https://doi.org/https://cordis.europa.eu/project /rcn/37577_en.xml.

Hluchanova, J. et al. 2012. “Solid Wastes Originated From Hot-Dip Galvanizing Process.” In *ISDM 2012 - FREIBERG*, 282–86.

Kekesi, Tamas et al. 2002. “The Purification of Base Transition Metal.” In *Purification Process and Characterization of Ultra High Purity Metals*. Berlin, Heidelberg: Springer.

Kekesi, Tamas. 2018. *The Fundamentals of Chemical Metallurgy*.

Kekesi et al. 2003. “Anion Exchange for Ultra-High Purification of Transition Metals.” *ERZMETALL* 56 (2): 59–67.

Kékesi, Tamás. 2002. “International Motivation and Cooperation for Research in the Ultra-High Purification of Metals.” *European Integration Studies* 1 (2): 109–26.

Kekesi, Tamas. et al. 2002. “Ultra-High Purification of Iron by Anion Exchange in Hydrochloric Acid Solutions.” *Hydrometallurgy* 63 (1): 1–13. https://doi.org/10.1016/S0304-386X(01)00208-0.

Kulcsar, T. et al. 2016. “Complex Evaluation and Development of Electrolytic Tin Refining in Acidic Chloride Media for Processing Tin-Based Scrap from Lead-Free Soldering.” *Transactions of the Institutions of Mining and Metallurgy, Section C: Mineral Processing and Extractive Metallurgy* 125 (4): 228–37. https://doi.org/10.1080/03719553.2016.1206693.

Regel-Rosocka, Magdalena. 2010a. “A Review on Methods of Regeneration of Spent Pickling Solutions from Steel Processing.” *Journal of Hazardous Materials* 177 (1–3): 57–69. https://doi.org/10.1016/j.jhazmat.2009.12.043.

San Román, M. F. et al. 2012. “Hybrid Membrane Process for the Recovery of Major Components (Zinc, Iron and HCl) from Spent Pickling Effluents.” *Journal of Membrane Science* 415–416:616–23. https://doi.org/10.1016/j.memsci.2012.05.063.

Sonmez et al. 2003. “A Study on the Treatment of Wastes in Hot Dip Galvanizing Plants.” *Canadian Metallurgical Quarterly* 42 (3): 289–300. https://doi.org/10.1179/cmq.2003.42.3.289.

Tang, Jianzhao. et al. 2016. “The Recycling of Ferric Salt in Steel Pickling Liquors: Preparation of Nano-Sized Iron Oxide.” *Procedia Environmental Sciences* 31: 778–84. https://doi.org/10.1016/j.proenv.2016.02.071.

Uchikoshi, Masahito. et al. 2004. “Production of Semiconductor Grade High-Purity Iron.” *Thin Solid Films* 461 (1): 94–98. https://doi.org/10.1016/j.tsf.2004.02.076.

Entrepreneurship in the Raw Materials Sector – Bartha et al. (Eds)

Author Index